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Rhenium Complexes Bearing Phosphole-Pyridine Chelates: Simple Molecules with Large Chiroptical Properties

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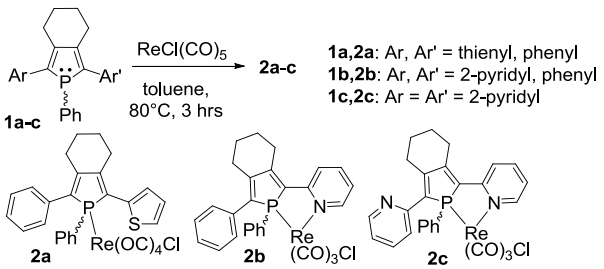
The synthesis and chiroptical properties of chiral rhenium complexes bearing mono- or di-topic phosphole ligands are described.

There is an increasing demand in developing chiral molecular materials[1a,b] in diverse domains such as molecular switches,[1c] circular polarized light (CPL) emitters,[1d] chiral metallogels and nanofibers,[1a] ... Further developments in these important domains require molecular engineering for developing easily accessible enantiopure molecules displaying large chiroptical properties, a task that is difficult to achieve using classical synthetic chemistry.[1,2] Coordination chemistry has been rarely used for this purpose although it offers a straightforward access to derivatives exhibiting appealing properties due to the presence of the metal atom.[1b] For example, it has been shown that the intrinsic nature of the rhenium ion (diverse coordination modes, large spin-orbit coupling, relativistic effects…) impacts the redox and optical properties of the corresponding Re^{I}(carbonyl)(diimine) complexes leading to numerous applications in solar chemistry, optoelectronics and photocatalysis.[3] However, up to now, few chiral Re^{I} complexes have been prepared,[4] and little attention has been paid on their chiroptical properties.[4d-i] In this paper, the synthesis, enantioresolution and optical properties of chiral rhenium complexes (**2a-c**, Scheme 1) bearing phosphole-based π-conjugated ligands behaving either as monotopic P-donors (**1a**, Scheme 1) or as ditopic 1,4-P,N chelates (**1b**,**c**) are described.[5,6]. The chiroptical properties, namely circular dichroism (CD) and optical rotation (OR), of these complexes are unexpectedly very large. This unprecedented coordination-driven molecular engineering offers a straightforward access to very simple molecules exhibiting large chiroptical properties.

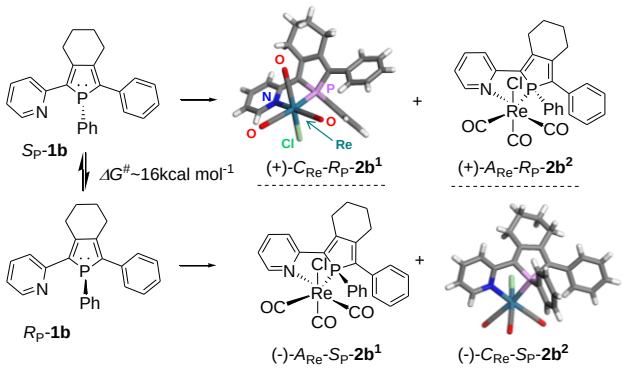
The target Re^{I}-complexes **2a-c** (Scheme 1) were prepared by reacting π-conjugated phospholes **1a-c**[5a,d] with $ReCl(CO)_5$ in toluene at 80°C under argon.[3] These air-stable compounds were purified by column chromatography over silica gel and isolated with moderate yields (55-60%). Their multinuclear NMR spectroscopy and mass spectrometry data support the proposed structures (see SI). For example, the formation of the five-membered metallacycles in **2a**,**c** upon coordination of the (2-pyridyl)phosphole moiety of **1a**,**c** results in a downfield ^{31}P NMR coordination chemical shifts (**2a**, +21.3 ppm; **2b**,**c**: +45.7/+50.7 ppm).[5d] The proposed structures were confirmed by an X-ray diffraction study on complex **2b** (*vide infra*).



Scheme 1. Synthesis of rhenium complexes **2a-c**.

It is worth noting that, although phospholes **1a-b** feature a P-chirogenic center, they cannot be isolated as single enantiomers due to the rapid P-inversion in solution (inversion barrier, ca. 16 kcal mol^{-1}).[6] Furthermore, symmetrical phosphole **1c** becomes chiral only upon coordination on the Re^{I}-center (Scheme 1). As a consequence, the isolation of enantiomerically pure derivatives was undertaken on complexes **2a-c**. Complex **2a** consists of a R_P/S_P enantiomeric mixture, which was resolved with *ee*'s higher than 98% by HPLC separations over a Chiralpak IA stationary phase (see SI). Complexes **2b**,**c** exist as four configurationally stable stereoisomers, observed by $^{31}P\{^{1}H\}$ NMR spectroscopy (**2b**, +47.7, +50.7; **2c**, +48.2, +45.7), due to the presence of two stereogenic centers (R_P/S_P, A_{Re}/C_{Re}). The four stereoisomers of complex **2b** were obtained with *ee*'s higher than 97% by chiral HPLC (Scheme 2). The two epimers of complex **2b** C_{Re}-R_p-**2b**^{1} and C_{Re}-S_p-**2b**^{2} were characterized by an X-ray diffraction study (Scheme 2). The Re^{I}-ions display a classic distorted octahedral geometry with the Cl-ligand occupying apical positions. The epimerization barrier of complex **2b** is high enough (ca. 27 kcal.mol^{-1} at 50°C, see SI) to prevent racemization to take place at room temperature. The enantiomers of complex **2c** were also obtained in high *ee*'s (> 98 %) by chiral HPLC, however the two epimers appear to have different configurational stability. The epimerization barrier of **2c**^{2} is rather low (~23 kcal mol^{-1} at 22°C), preventing its chiroptical properties to be examined, while

enantiomers **2c**[1] are stable enough to be investigated by CD spectroscopy. Indeed, a family of configurationally stable chiral (phosphole-pyridine)Re[I]-complexes **2b**[1,2]-**2c**[1] (Figure 1) with various π-conjugated framework have been synthesized.



Scheme2. Stereochemical aspects of complex **2b**. Molecular structures of **2b**[1,2] determined by X-ray crystallography. For *A*/*C* stereochemical assignments see reference 1b.

The UV-vis spectra of rhenium complexes **2a-c** display a large absorption band tailing down to 500 nm (Figure 1). Note that, according to the X-Ray diffraction study performed on **2b**[1,2], the twist angle between the coordinated pyridine and phosphole ring (CCCC dihedral angle, +51.0°±2°) is within classical range[2b,5d] and allow efficient π-conjugation along the sp[2]-carbon backbone. According to PBE0 DFT and TD-DFT calculations using a polarized LanL2DZ basis set, the lowest energy transition of complex **2b**[2] is essentially (>96%) an HOMO–> LUMO transition. The HOMO spans from the Cl-Re-CO fragment to the phosphole ring and the LUMO is essentially spread over the pyridyl-phosphole moiety (Figure 1), showing that this transition is a metal-ligand to ligand charge transfer (MLLCT).

The complex **2a** is fluorescent at room temperature (λ_{em}= 518 nm), which is ligand-centered according to theoretical calculation, whereas **2b**,**c** displayed no luminescence properties. The experimental CD spectra of complexes **2a-c** were recorded in CH_2Cl_2 (5×10^{-5} M). The CD spectrum of (+)-**2a** shows several bands with small $\Delta\varepsilon$ values (Figure 2). The CD spectra of complexes **2b**[1,2] and **2c**[1] display a similar general shape with a broad positive CD band between 330 and 430 nm ($\Delta\varepsilon \sim$ 15-22 M^{-1} cm^{-1}) and a negative one around 280 nm ($\Delta\varepsilon \sim$ -40 to -20 M^{-1} cm^{-1}) for the (+) enantiomers (Figure 2). The only noticeable difference is observed at ca. 310 nm, the smaller CD band have opposite sign for (+)-**2b**[1] and (+)-**2b**[2], while for (+)-**2c**[1] this band is almost vanishing. It is noteworthy that the CD bands complexes **2b**[1,2] and **2c**[1] featuring π-conjugated (2-pyridine)phosphole chelates are relatively intense for small molecules, and especially compared to complex **2a** bearing a monodentate phosphole ligand (Figure 2). Indeed, complex **2a** displays optical rotations equal to zero. In marked contrast, Re[I]-complexes **2b**[1,2] and **2c**[1] exhibit specific rotations $[\alpha]_D^{23}$ between 520-625 and molar rotations $[\phi]_D^{23}$ between 3200-4240 (Table 1). These values are surprisingly large, almost the same order of magnitude as helicenes molar rotations,[2] and deserve to be examined in more details.

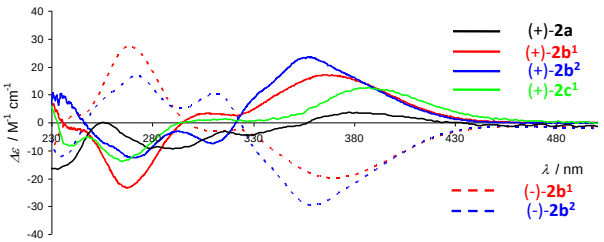


Figure2. Circular dichroism spectra of complexes (+)-**2a**, (+)/(-)-**2b**[1], (+)/(-)-**2b**[2] and (+)-**2c**[1].

PBE0 TD-DFT calculations using an extended basis set well-reproduce the CD shape of diastereomeric complexes **2b**[1,2] and **2c**[1] and enabled to assign their absolute configurations ((+)-C_{Re}-R_P-**2b**[1]; (+)-A_{Re}-R_P-**2b**[2], Scheme 2, (+)-C_{Re}-R_P-**2c**[1]) (see SI). These absolute configuration assignments were further confirmed by X-ray crystallography of (+)-C_{Re}-R_P-**2b**[1] and (-)-C_{Re}-S_P-**2b**[2] (Scheme 2). The fact that complexes **2b**[1,2] and **2c**[1] show large chiroptical properties may be explained by analyzing the MO's involved in the low energy CD-active electronic transitions that significantly contribute to the molar rotations.

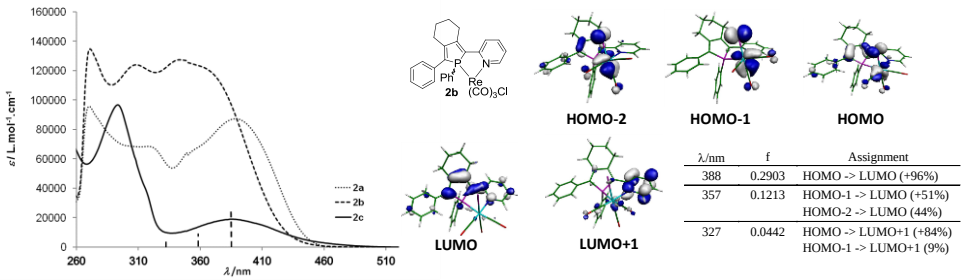


Figure 1. Absorption spectra of **2a-c** in CH_2Cl_2, TD-DFT simulated spectrum and molecular orbitals for diastereoisomer **2b**[2] (vertical dashed lines).

Indeed, the HOMO-LUMO transition in **2a** involves the π-conjugated system centered on the phosphole ligand *only*, with a marginal participation of the rhenium atom (see SI). Such transition has a small rotational strength and may account for the zero optical rotation value for **2a**. On the contrary, the positive CD-active band at 380-400 nm in

(+)-**2b**[1] is a HOMO-LUMO transition with a high charge transfer character (MLLCT, Figure 1) and a substantial rotational strength since it involves a highly dissymmetric environment around the rhenium atom and the 1,4-P,N chelate. Relativistic effects may also affect the optical rotation, because 5d/6s orbitals in 5d metals hybridize better than 4d/5s orbitals in 4d metals. Note that the sign of the optical rotation is determined by the stereochemistry at the phosphorus center (R_P-(+) and S_P-(-)). The same conclusions can be drawn for complex **2c**[1], for which the CD active band at ~380 nm involves the HOMO-2 to LUMO+1 orbitals, that are respectively metal-ligand centered and ligand centered (see SI). These last results highlight the fact that large molar rotations and CD values can be obtained upon complexation of the N,P-moiety of a symmetrical molecule such as the bis(2-pyridyl)phosphole **1c** (Scheme 1).[5c,d]

Table 1. Experimental specific and molar rotations of enantio-enriched compounds **2b**[1,2] and **2c**[1] enantiomers.

	(-)-2b[1]	(+)-2b[1]	(-)-2b[2]	(+)-2b[2]	(-)-2c[1]	(+)-2c[1]
$[\alpha]_D^{23}$ [a,b]	-625	+570	-520	+480	-555	+500
$[\phi]_D^{23}$ [a,d]	-4240	+3860	-3510	+3205	-3740	+3370

[a] 0.01 g/100mL in CH_2Cl_2. Measured. [b] In deg cm^2 dmol^{-1} and within an error of ±10%.

In conclusion, we have shown that optically active Re^I complexes bearing 2-pyridyl-phosphole P,N exhibit surprisingly large chiroptical properties originating from *i*) the presence of the heavy metal, *ii*) the large dissymmetric environment about the metal center, and *iii*) the π-conjugated nature of the (2-pyridyl)phosphole ligands. This molecular engineering based on coordination of π-conjugated phosphole-pyridine ligands on heavy metal atoms opens a new route for the easy synthesis of simple molecules with appealing chiroptical behavior.

Notes and references

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† Electronic Supplementary Information (ESI) available: [Experimental section, theoretical calculations, spectroscopic data, X-ray crystallographicdata and a CIF files]. See DOI: 10.1039/b000000x/

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